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LETTER

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Additive Effect of *N*-Heteroaromatics on Transesterification Catalyzed by Tetranuclear Zinc Cluster

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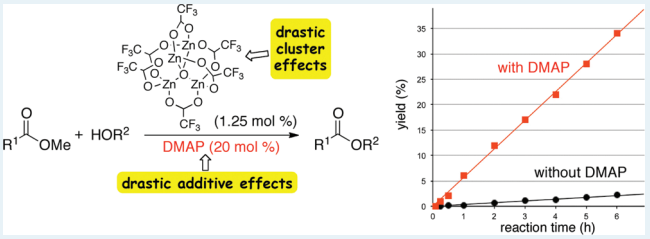
Supporting Information

ABSTRACT: A catalytic amount of 4-dimethylaminopyridine showed drastic additive effects on transesterification catalyzed by the μ_4-oxo-tetranuclear zinc cluster $Zn_4(OCOCF_3)_6O$, enhancing the catalytic activity by more than 15-fold. The new catalyst system facilitates transesterification of less reactive sterically demanding esters and alcohols.

KEYWORDS: Zinc, catalysis, transesterification, cluster, additive effects, DMAP



Catalytic transesterification is one of the most desirable reactions for synthesizing diverse esters in terms of atom-economy, practicality, substrate generality, and functional group tolerance.[1−4] Although several efficient catalysts,[5−22] such as $Ti(OR)_4$,[5,15] $Al(OR)_3$,[6,8] and distannoxane,[7,17,18,20] have been reported, recent development has focused on searching for catalysts that are active not only under mild conditions[23−26] but also for sterically demanding substrates whose transesterification has been difficult.[11,12,16,22,26−29] We recently reported that the μ_4-oxo-tetranuclear zinc cluster $Zn_4(OCOCF_3)_6O$ (**1a**)[30−36] serves as an efficient catalyst for the transesterification. The advantages of **1a** were its high functional group tolerance to acid-sensitive groups, such as THP and TES ethers, and a unique chemoselectivity that predominantly acylated a hydroxyl group in the presence of much more nucleophilic primary and secondary alkylamines.[31,34] Herein, we report significant accelerating effects of alkylamines and *N*-heterocyclic compounds on the tetranuclear Zn cluster-catalyzed transesterification. The addition of 4-dimethylaminopyridine (DMAP) dramatically enhanced the catalytic activity for transesterification (more than 15-fold) and achieved the transesterification of less reactive sterically demanding esters and alcohols. Moreover, experimental results, kinetic studies, and ESI-MS analysis suggested that DMAP coordinates to zinc ion and stabilizes more catalytically active clusters with lower nuclearities, presumably dinuclear Zn_2 or trinuclear Zn_3 species.

RESULTS AND DISCUSSION

Transesterification of sterically demanding substrates remains a difficult and challenging task because of the low reactivity.[1−4] During the course of our studies on the chemoselective acylation of hydroxyl groups over amino groups,[31,34] we discovered important clues to solving this problem. In the presence of an equivalent amount of cyclohexylamine (**4a**), for example, the acylation of cyclohexyl alcohol (**3a**) with methyl 3-phenylpropanoate (**2a**) provided the corresponding ester in 94% yield after refluxing for 18 h, whereas in the absence of amine **4a**, the reaction provided the same product in only 22% yield, even after refluxing for 48 h (Scheme 1). These results clearly indicate that under this acylation condition, highly nucleophilic alkylamine, which is in general acylated in preference to alcohol, greatly accelerates the acylation of alcohol without being converted to the corresponding amide. Further, the addition of only a catalytic amount of alkylamine (20 mol %) was sufficient to achieve satisfactory catalyst activity (see the Supporting Information).

Encouraged by such drastic additive effects of **4a**, we next examined a variety of amine additives (Table 1, entries 1−11). Other sterically *unhindered* primary amines—1-hexylamine (**4b**) and 4-heptylamine (**4c**)—also had significantly positive effects, but *tert*-butylamine (**4d**) had only moderate effects, probably due to its steric hindrance. Secondary alkylamines piperidine (**4e**), pyrrolidine (**4f**), and dipropylamine (**4g**) were also good additives, but tertiary and aromatic amines had only limited effects (entries 9−11). Notably, no amide formation was detected in the reactions with amine additives. On the basis of the fact that metal ions in the active site of some metalloenzymes such as aminopeptidase are supported by both carboxylate and imidazole ligands,[37−40] we further examined heteroaromatics as additives (entries 12−22). Although the addition of imidazole (**6c**), pyrazole (**6e**), and HOBt (**6f**) completely inhibited the reaction and the addition of pyrrole (**6a**) and indole (**6b**) had almost no effect, 1-methylimidazole (**6d**)[41] markedly increased the yield to

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Scheme 1. Effects of Amine 4a on Transesterification

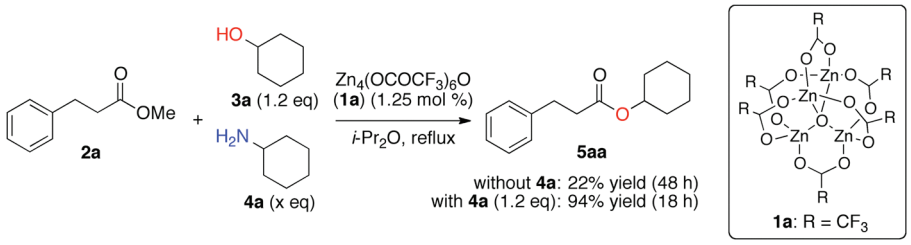
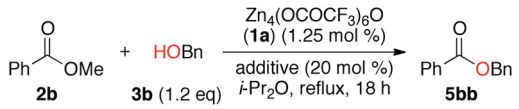
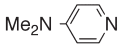
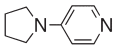


Table 1. Screening of Amine and Heteroaromatic Additives[a]



entry	additive		yield (%)[b]
1	–		21
2	*c*-HexNH$_2$	(**4a**)	90
3	*n*-HexNH$_2$	(**4b**)	91
4	(*n*-Pr)$_2$CHNH$_2$	(**4c**)	89
5	*t*-BuNH$_2$	(**4d**)	47
6	piperidine	(**4e**)	77
7	pyrrolidine	(**4f**)	89
8	(*n*-Pr)$_2$NH	(**4g**)	72
9	Et$_3$N	(**4h**)	28
10	PhNH$_2$	(**4i**)	38
11	PhNMe$_2$	(**4j**)	22
12		(**6a**)	19
13		(**6b**)	19
14		(**6c**)	trace
15		(**6d**)	81
16		(**6e**)	n.d.[c]
17		(**6f**)	n.d.[c]
18		(**6g**)	60
19		(**6h**)	92
20		(**6i**)	83
21		(**6j**)	30
22		(**6k**)	17

[a] All data are the average of two experiments. [b] Yield was determined by GC analysis. [c] Not detected.

81%, suggesting that the presence of rather acidic N−H or O−H protons retards the reaction and *N*-heteroaromatics accelerate the reaction rate. Furthermore, pyridine (**6g**) had moderate effects, and more nucleophilic DMAP (**6h**)[42,43] and 4-pyrrolidinopyridine (**6i**)[44] afforded excellent yields of 92% and 83%, respectively. Other types of heteroaromatics, such as furan (**6j**) and thiophene (**6k**), were not effective.

We performed the reactions of **2b** and **3a** with various amounts of DMAP (**6h**) (Figure 1, left). Yield of the product **5ba** dramatically increased with an increase of **6h** in the range of 0−20 mol %. Although the reaction with 40 mol % of **6h** gave a little better result, we determined 20 mol % loading of **6h** as an optimized condition in terms of atom economy. Time-course for the reaction in the presence of the best alkylamine-type additive **4a** and the best *N*-heterocycle-type additive **6h** revealed that the addition of 20 mol % of these additives increased the initial rate of the reactions more than 3- and 15-fold, respectively (Figure 1, right). The addition of these additives at any stage of the reaction sufficiently accelerated the reaction.

With the best additive, DMAP, in hand, we investigated the substrate generality of the transesterification of comparatively low reactive esters as well as alcohols. As shown in Table 2, DMAP had drastic positive effects on the reaction, resulting in great improvement of the chemical yield (up to 98%). The reactions of methyl 2-methylbenzoate (**2c**) (entry 1, 89%), methyl 4-methoxybenzoate (**2d**) (entry 2, 89%), methyl cyclohexanecarboxylate (**2e**) (entry 3, 98%), and highly congested methyl 1-adamantanecarboxylate (**2f**) (entry 4, 94%) with 1-butanol (**3c**) in the presence of 20 mol % DMAP resulted in satisfactory yields, although sluggish reactions were observed for the corresponding substrates in the absence of the additive. The DMAP additive system was also superior for the less reactive alcohols (entries 5−8). The reactions of methyl 3-phenylpropanoate (**2a**) with cyclohexanol (**3a**), 4-heptanol (**3d**), 1-indanol (**3e**), and D-menthol (**3f**) afforded the corresponding products in high yields (83−93%). Notably, the addition of DMAP not only accelerated the catalytic rate but also suppressed undesirable side reactions because of the neutral reaction conditions; the reaction of **2a** with 1-indanol (**3e**) afforded the product 1-indanyl 3-phenylpropanoate (**5ae**) in 88% yield, despite observations that the same reaction conducted in the absence of DMAP resulted in a complex mixture of decomposed products from **3e** via a carbocation intermediate (entry 7).[45−47]

The DMAP (**6h**) additive effect on the transesterification of methyl benzoate (**2b**) with cyclohexanol (**3a**) was exemplified by using various zinc sources, leading to the discovery of a drastic cluster effect[11,12,48−56] to accelerate the reaction rate using **1a**. As shown in Table 3, the sufficiently increased yield (93%) of cyclohexyl benzoate (**5ba**) was obtained for the Zn cluster catalyst **1a** (entry 1), as compared with a controlled reaction (entry 2, 5% yield). Although positive additive effects of **6h** were observed in all cases, other zinc sources, including Zn(OCOCF$_3$)$_2$, did not produce satisfactory results. In addition, the combination of Zn$_4$(OCOCH$_3$)$_6$O (**1b**) and **6h** showed much lower reactivity (entry 5, 10% yield), indicating that the Lewis acidity of the catalyst was also an important factor for the catalytic activity. In

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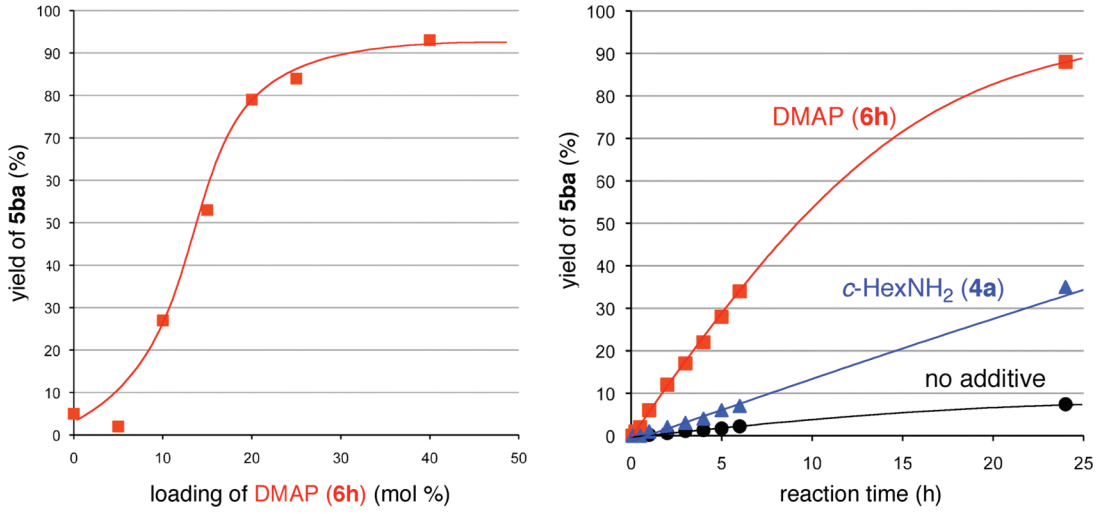
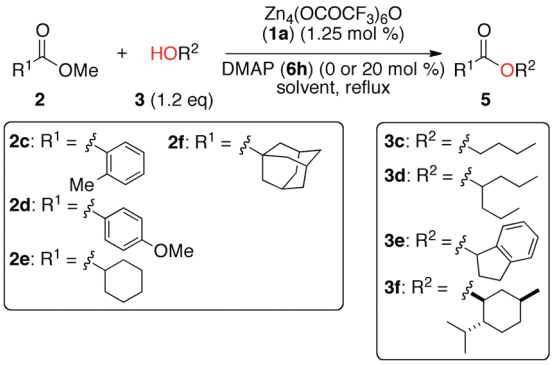


Figure 1. (left) Transesterification with various amounts of DMAP (**6h**). (right) Time-course for the **1a**-catalyzed transesterification of **2b** with **3a** in the presence of 20 mol % of **4a** (blue up-facing triangle), 20 mol % of **6h** (red solid box) or in the absence of additives (black circle).

Table 2. Additive Effects on the 1a-Catalyzed Transesterification: Scope and Limitations



entry	2	3	solvent	time (h)	yield (%)[a] without DMAP	yield (%)[a] with DMAP
1	**2c**	**3c**	toluene	48	2	89
2	**2d**	**3c**	toluene	18	7	89
3	**2e**	**3c**	*i*-Pr_2O	18	25	98
4	**2f**	**3c**	toluene	90	trace	94
5	**2a**	**3a**	toluene	18	58	92
6	**2a**	**3d**	*i*-Pr_2O	48	38	93
7	**2a**	**3e**	*i*-Pr_2O	18	5[b]	88
8	**2a**	**3f**	*i*-Pr_2O	72	23	83

[a] Isolated yield. [b] A complex mixture of products was obtained.

the presence of **6h** without the zinc sources, product **5ba** was not detected at all (entry 11).[23,57]

To gain insight into the mechanism of **1a**-catalyzed transesterification and effects of DMAP, we first performed ESI-MS analysis. Measurements of **1a** on ESI-MS revealed some peaks assignable to mononuclear "Zn", dinuclear "Zn_2", and trinuclear "Zn_3" species, in addition to "Zn_4" and its higher-nuclear species, such as "Zn_5" and "Zn_6" clusters. With the increase of DMAP additive, relative intensities of "Zn_4" species and its higher-nuclear species decreased, and those of DMAP-coordinated lower-nuclear Zn species "Zn_n-$(dmap)_m$ (n = 1∼3)" greatly increased, indicating that DMAP enhanced the cleavage of **1a** to give cluster species with lower nuclearities. ^{1}H NMR analysis also suggested the coordination of DMAP to Zn ions (see the Supporting Information).

Next, kinetic studies were conducted using the transesterification of phenyl benzoate (**7**) with 1-hexanol (**3g**) because, once generated, phenol did not react with the resulting hexyl benzoate (**5bg**),[32,35] preventing the reverse reaction (eq 1). Under the pseudo-first-order condition of excess amounts of **7** and **3g**, we determined that the reaction order in the catalyst **1a** was 0.52 (the rate law for the reaction can be expressed as $d[\mathbf{5bg}]/dt = k[\mathbf{7}]^{0.98}[\mathbf{3g}]^{0.66}[\mathbf{1a}]^{0.52}$). These results strongly suggested that several zinc clusters existed in equilibrium in the

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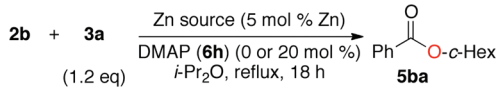
Table 3. Effects of Zn Source with DMAP (6h) additive[a]



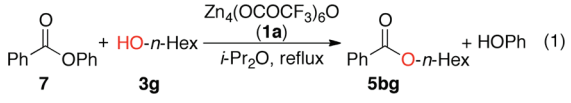
entry	Zn source	additive	yield (%)[b]
1	$Zn_4(OCOCF_3)_6O$ (**1a**)	DMAP (**6h**)	93
2	$Zn_4(OCOCF_3)_6O$ (**1a**)		5
3	$Zn(OCOCF_3)_2$	DMAP (**6h**)	24
4	$Zn(OCOCF_3)_2$		7
5	$Zn_4(OCOCH_3)_6O$ (**1b**)	DMAP (**6h**)	10
6	$Zn_4(OCOCH_3)_6O$ (**1b**)		1
7	$Zn(OCOCH_3)_2$	DMAP (**6h**)	trace
8	$Zn(OCOCH_3)_2$		trace
9	$Zn(OTf)_2$	DMAP (**6h**)	2
10	$Zn(OTf)_2$		trace
11		DMAP (**6h**)	n.d.[c]

[a] All data are the average of two experiments. [b] Yield was determined by GC analysis. [c] Not detected.

reaction mixture, and zinc clusters with lower nuclearities had significantly higher catalytic activity than those with higher nuclearities, including Zn_4 species.

In the presence of 20 mol % of DMAP, we also performed a kinetic study and observed that the rate law obeyed the 0.41 order of catalyst **1a**, again suggesting equilibrium of several zinc species and the high catalytic activity of clusters with lower nuclearities. The reaction order in DMAP was rather complicated but had a tendency to be small (~0.6 → 0.3) with increased concentration of DMAP. This kinetic data and the results shown in Figure 1, together with the above-mentioned ESI-MS analysis and NMR study, indicate that DMAP coordinates to zinc ion until a certain ratio of DMAP to Zn and stabilizes more catalytically active clusters with lower nuclearities.

Accordingly, we conducted controlled experiments to rule out the possibility that any mononuclear Zn species bearing DMAP acted as a catalytically active species. We thus synthesized a mononuclear complex, $Zn(OCOCF_3)_2(dmap)_2$ (**8**), by treating $Zn(OCOCF_3)_2$ with 2 equiv of DMAP in diisopropyl ether, and the complex **8** was characterized by NMR spectroscopy and X-ray analysis. Notably, mononuclear complex **8** had almost no catalytic activity for the transesterification of **2b** with **3a**. Although the exact structure of the active species remains unclear, on the basis of the above-mentioned results, we propose that dinuclear species "Zn_2-$(dmap)_m$" or trinuclear species "Zn_3-$(dmap)_m$", or their equilibrium mixture, generated from tetranuclear zinc cluster **1a** is a more active species as compared with **1a** and other DMAP-free zinc species, including dinuclear "Zn_2" and trinuclear "Zn_3" species.



Another possible role of DMAP (**6h**) could be the in situ generation of a highly reactive acyl pyridinium salt from ester **2**, as in the well-established reaction of acyl halides or anhydrides with **6h**.[58,59] The Zn cluster **1a**-catalyzed transesterification with the **6h** additive, however, proceeded in a highly O-selective manner, despite the N-selective feature of acyl pyridinium salt. Together with the fact that acyl pyridinium salt was not detected in the reaction mixture by ^{1}H NMR or ESI-MS, it seems unlikely that the reaction proceeds via acyl pyridinium salt. The above-mentioned kinetic data also suggests that the in situ generation of the acyl pyridinium salt is not a major role of **6h**.

CONCLUSION

We succeeded in greatly improving the catalytic activity of the tetranuclear zinc cluster **1a**-catalyzed transesterification by adding a catalytic amount of DMAP. The addition of DMAP stabilized the clusters with lower nuclearities and enhanced catalytic activity for transesterification. Moreover, less reactive sterically demanding substrates could be catalyzed by the newly developed catalyst system of **1a** and DMAP. Further studies on the precise reaction mechanism are in progress.

ASSOCIATED CONTENT

Supporting Information. Experimental procedures, characterization of the products, and other detailed results (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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